

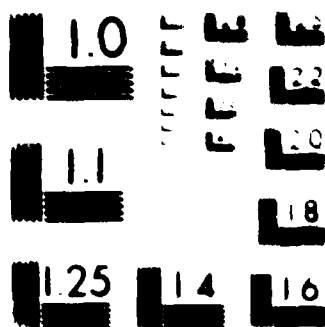
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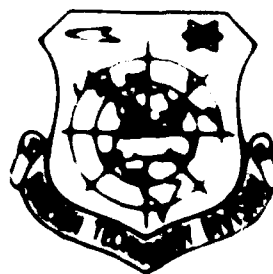


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# PARTIALLY EDITED MACHINE TRANSLATION

FTD-ID(RS)T-0844-87

3 September 1987

MICROFILM NR: FTD-87-000007-01

RUSS-MOLECULAR COMPOUNDS (Selected Articles)

English pages: 21

Source: Vysokomolekulyarnye Soedineniya, Seriya B, Kratkoye Soobshcheniya, Vol. 14, Nr. 4, April 1972, pp. 292-295; 311-314

Country of origin: USSR

This document is a machine translation.

Input and Merged by: Pamela A. Bricker

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Foreign Page # \_\_\_\_\_

Incorrect word/phrase: \_\_\_\_\_

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Foreign page numbers occur in the English text and may be found anywhere along the left margin of the page as in this example:

In them occurs the state named "night blindness" - hemeralopia, which, according to the current point of view, is a result of damage of the rod-shaped apparatus of the eye.

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However, in recent years it has been shown that with the hereditary pigment degenerations in animals the biochemical changes are observed in all cellular elements of the retina.

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# U. S. BOARD ON GEOGRAPHIC NAMES transliteration SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
1	<b>А а</b>	A, a	11	<b>Р р</b>	R, r
2	<b>Б б</b>	B, b	12	<b>С с</b>	S, s
3	<b>В в</b>	V, v	13	<b>Т т</b>	T, t
4	<b>Г г</b>	G, g	14	<b>У у</b>	U, u
5	<b>Д д</b>	D, d	15	<b>Ф ф</b>	F, f
6	<b>Е е</b>	Y, y; E, e*	16	<b>Х х</b>	KH, kh
7	<b>Ж ж</b>	Zh, zh	17	<b>Ц ц</b>	Ts, ts
8	<b>З з</b>	Z, z	18	<b>Ч ч</b>	Ch, ch
9	<b>И и</b>	I, i	19	<b>Ш ш</b>	Sh, sh
10	<b>Я я</b>	Y, y	20	<b>Щ щ</b>	Shch, shch
	<b>К к</b>	K, k	21	<b>Ъ ъ</b>	"
	<b>Л л</b>	L, l	22	<b>Ы ы</b>	Y, y
	<b>М м</b>	M, m	23	<b>Ь ь</b>	"
	<b>Н н</b>	N, n	24	<b>Э э</b>	E, e
	<b>О о</b>	O, o	25	<b>Ю ю</b>	Yu, yu
	<b>П п</b>	P, p	26	<b>Я я</b>	Ya, ya

\*ye initially, after vowels, and after o, e elsewhere.  
When written as ё in Russian, transliterate as yë or ë.

## RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh <sup>-1</sup>
cos	cos	ch	cosh	arc ch	cosh <sup>-1</sup>
tg	tan	th	tanh	arc th	tanh <sup>-1</sup>
ctg	cot	cth	coth	arc cth	coth <sup>-1</sup>
sec	sec	sch	sech	arc sch	sech <sup>-1</sup>
cosec	csc	csch	csch	arc csch	csch <sup>-1</sup>

Russian English

rot curl  
lg log

## GRAPHICS DISCLAIMER

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Page 292.

# THE MICRO-TACT OF POLYPHENYLMETHACRYLATE.

E. Yun, L. B. Stroganov, V. A. Agasandyan, A. D. Litmanovich, N. A. Plate.

Polyphenylmethacrylate (PFMA) is very convenient object for studying effect of adjacent links in reaction of hydrolysis of ethers/esters of polymethacrylic acid. Since reactivity of polymethacrylates depends on their micro-tact [1], during the kinetic investigations of hydrolysis it is desirable to study polymeric samples with different micro-tact. In this work by the method NMR was studied the micro-tact of the samples PFMA, synthesized by different methods.

## Experimental part.

Phenylmethacrylate (FMA) they synthesized from methacrylylchloride and phenol [2]; boiling point 83-84°/4 mm,  $n_D^{20}$  1.515.

Toluene, hexane, benzene, diethyl ether, dioxane, chloride butyl [3], ethyl bromide [4] purified by usual methods.

Pyrrole dried 24 hrs above CaH, and they distilled in current of argon above drier [5]; boiling point of 129-130°,  $n_D^{20}$  1.5085.

Piperidine was boiled during 3 hours and they distilled above solid KOH, then 24 hrs above CaH<sub>2</sub>, were dried and they accelerated/dispersed in current of argon [5]; boiling point of 104°,  $n_D^{20}$  1.4530

Butyllithium was prepared in hexane from chloride butyl and metallic Li [6]. The concentration of the prepared catalyst was determined by the method of dual titration [7].

Catalysts - dipyrrolyl magnesium  $Mg(\text{pyr})_2$  and dipiperidyl magnesium  $Mg(\text{piper})_2$  synthesized according to reaction  $Mg(C_2H_5)_2$ , with appropriate amine [5]. Diethylmagnesium was obtained by addition to solution  $C_2H_5MgBr$  in ether/ester (0.3 mole/l) of the solution of dioxane in ether/ester (4 mole/l) by three portions with the daily interval between the portions for the purpose of an increase in output/yield  $Mg(C_2H_5)_2$ , [8]. The solution, which contains  $Mg(C_2H_5)_2$ , crushed by argon into the flask/bulb. Sulfur ether and dioxane were distilled in the vacuum, the fallen precipitate  $Mg(C_2H_5)_2$ , was finished to the fixed weight by lyophilic drying. In the two-neck flask/bulb with a capacity of 50 ml, thoroughly "annealed" and blown-off by argon, were placed 0.01 moles  $Mg(C_2H_5)_2$ , and 15 ml of absolved toluene. To the formed suspension during the mixing 0.02 moles of piperidine or pyrrole at room temperature gradually were added. On the stop of the liberation/precipitation of ethane the solution was heated to the boiling point of solvent and was finished reaction to

the end. On cooling of system toluene to the total volume of 20 ml was added in the current of argon.

Benzoyl peroxide after washing by distilled water was dissolved in chloroform and then deposited by methanol. Recrystallized thus peroxide was dried in the vacuum at room temperature.

Anionic polymerization was conducted in three-necked flask/bulb with capacity of 0.5 l, preliminarily "annealed" in current of argon. In the flask/bulb loaded purified FMA, thoroughly dried above CaH<sub>2</sub>, and distilled in the vacuum directly before experiment, and toluene, distilled in the vacuum above the crystalline ethyl lithium. On the achievement of the temperature of polymerization the appropriate catalyst was introduced in the current of argon. In all cases after 15-20 min. from the solution into the precipitate the polymer settled. After the required for the polymerization time reaction they broke by the addition of methanol. The reprecipitation of polymer was conducted from the benzene either into methanol or into the petroleum ether. Samples were finished to the fixed weight in the vacuum at 50°.

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Radical polymerization of FMA conducted in ampules at 60° in medium of benzene; initiator - benzoyl peroxide.

Hydrolysis of samples PFMA, obtained under varied conditions, was

conducted in concentrated sulfuric acid. In the ampule, blown-off by argon, were loaded by 0.3-0.5 g of polymer, 6 ml  $H_2SO_4$ , and 3 drops  $H_2O$ . After 24 hours they poured out homogeneous mixture into the ice water. Precipitate they centrifuged and they dried by lyophilic drying. The obtained polymethacrylic acid they converted into the polymethyl methacrylate (PMMA) by methylation in the medium of benzene by diazomethane [9]. The depth of hydrolysis and the completeness of methylation were controlled with the aid of IR spectroscopy [10].

#### Results and their discussion.

NMR spectra were removed/taken at  $175^\circ$  and frequency of 60 MHz on instrument C-60HL of firm JEOL. For the measurements 10% solutions of polymers in the o-dichlorobenzene, which contains 1% of octamethylcyclotetrasiloxane (internal standard), were used. The spectra of samples PFMA (Fig. 1) qualitatively coincided with the spectra of samples PFMA, described earlier [11]. Due to the large spectral line width it was impossible to carry out the quantitative analysis of the micro-tact of the obtained samples; therefore conclusions about micro-tact of PFMA were made on the basis of the study of the NMR spectra of the corresponding samples PMMA, obtained as a result of hydrolysis and methylation (Fig. 2).

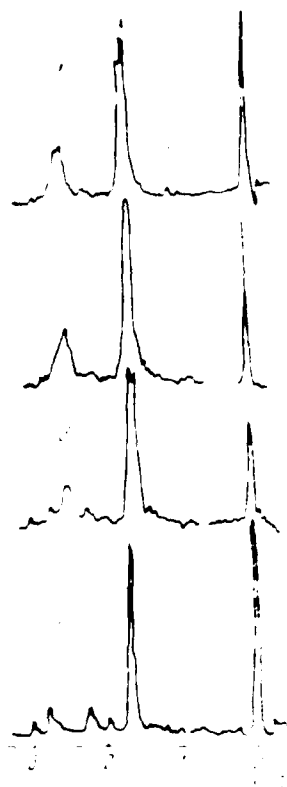


Fig. 1.

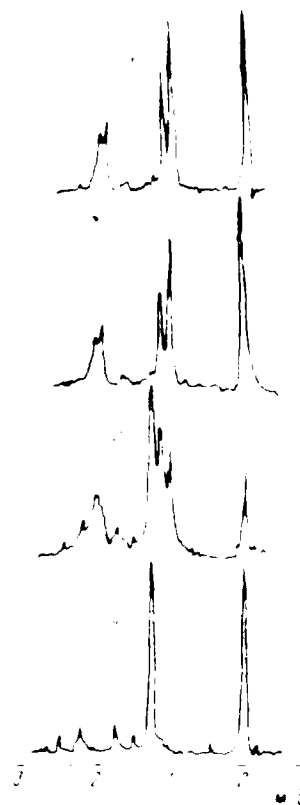


Fig. 2.

Fig. 1. NMR spectra of samples PFMA, obtained with benzoyl peroxide (1),  $\text{Mg}(\text{N} \text{---} \text{C}_6\text{H}_5)_2$  (2),  $\text{Mg}(\text{N} \text{---} \text{C}_6\text{H}_5)_2$  (3) and butyllithium (4).

Key: (1) ppm.

Fig. 2. NMR spectra of samples of polymethyl methacrylate, obtained from appropriate samples PFMA. Designations are the same as in Fig. 1.

Key: (1). ppm.

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For quantitative analysis of micro-tact they approximated line of

resonance absorption of  $\alpha$ -methyl protons  $F(x)$  (Fig. 3) by sum of three standardized/normalized Lorentz lines according to equation (1)

$$F(x) = \frac{\tilde{I}}{1 - \left(\frac{x - x_I}{\delta}\right)^2} + \frac{\tilde{H}}{1 - \left(\frac{x - x_H}{\delta}\right)^2} + \frac{\tilde{S}}{1 - \left(\frac{x - x_S}{\delta}\right)^2} \quad (1)$$

Here  $x_I$ ,  $x_H$  and  $x_S$  - chemical shifts of the  $\alpha$ -methyl protons of central links iso-, the hetero- and syndiotactic triads with respect [12] <sup>1</sup>;  $\tilde{I}$ ,  $\tilde{H}$  and  $\tilde{S}$  - values, proportional to the concentrations of such links, and  $\delta$  - spectral line half-width on the half-height (it is considered identical for all three lines).

FOOTNOTE <sup>1</sup>. With the strong overlap of spectral lines maximums  $F(x)$  cannot coincide with the actual values of chemical shifts  $x_I$ ,  $x_H$ ,  $x_S$ . However, during permission/resolution reached in this work the distances between the abscissas of maximums  $F(x)$  in the units of chemical shifts in accuracy coincided with differences in the literary values of chemical shifts;  $x_I - x_H$  and  $x_I - x_S$ . Therefore as  $x_I$ ,  $x_H$  and  $x_S$  were used chemical shifts of the corresponding maximums  $F(x)$ .  
ENDFOOTNOTE.

$\tilde{I}$ ,  $\tilde{H}$  and  $\tilde{S}$  found as follows. In equation (1) substituted the value of  $x$  and  $F(x)$ , that correspond to the coordinates of maximums  $F(x)$ , and also  $\delta_0$  - half-width of lines on the half-height of the more permitted peak. As a result was obtained the system of three linear equations with three unknowns  $\tilde{I}$ ,  $\tilde{H}$  and  $\tilde{S}$ , whose solution gave zero approximation to the content of iso-, hetero- and syndiotriads:  $\tilde{I}_0$ ,  $\tilde{H}_0$  and  $\tilde{S}_0$ .

Substituting these values together with  $\delta_0$  into equation (1), were calculated values of  $F(x)$  at points of minima  $x_1$  and  $x_2$  (Fig. 3). The comparison of the calculated values  $F(x_1)$  and  $F(x_2)$  with the experimentally observed values made it possible to make a conclusion about how it is necessary to change  $\delta$  for the best coordination with the experiment. After the selection of new value  $\delta(\delta_1)$  the procedure of calculation was repeated. Process was continued until the effectiveness of iteration sharply decreased. Thus found the standardized/normalized to one values  $I$ ,  $H$ ,  $S$  and  $\delta$  (table). Using these values, according to equation (1) there were determined values  $F(x)$  (Fig. 3). As can be seen from the figure, the calculated points coincide sufficiently well with the real spectral line.



Fig. 3. Diagrammatic representation of the resonance assignments of  $\alpha$ -methyl protons (explanation in text).

**Key:** 1234567890

Conditions of polymerization of FMA and the nature of the resulting polymers.

№ п/п	Наименование	Единица измерения	Количество	Стоимость	Сумма
1	Персональный кабинет	шт.	1	1000000	1000000
2	Диван	шт.	1	1000000	1000000
3	Диван	шт.	1	1000000	1000000
4	Диван	шт.	1	1000000	1000000
5	Диван	шт.	1	1000000	1000000
6	Диван	шт.	1	1000000	1000000
7	Диван	шт.	1	1000000	1000000
8	Диван	шт.	1	1000000	1000000
9	Диван	шт.	1	1000000	1000000
10	Диван	шт.	1	1000000	1000000
11	Диван	шт.	1	1000000	1000000
12	Диван	шт.	1	1000000	1000000
13	Диван	шт.	1	1000000	1000000
14	Диван	шт.	1	1000000	1000000
15	Диван	шт.	1	1000000	1000000
16	Диван	шт.	1	1000000	1000000
17	Диван	шт.	1	1000000	1000000
18	Диван	шт.	1	1000000	1000000
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27	Диван	шт.	1	1000000	1000000
28	Диван	шт.	1	1000000	1000000
29	Диван	шт.	1	1000000	1000000
30	Диван	шт.	1	1000000	1000000
31	Диван	шт.	1	1000000	1000000
32	Диван	шт.	1	1000000	1000000
33	Диван	шт.	1	1000000	1000000
34	Диван	шт.	1	1000000	1000000
35	Диван	шт.	1	1000000	1000000
36	Диван	шт.	1	1000000	1000000
37	Диван	шт.	1	1000000	1000000
38	Диван	шт.	1	1000000	1000000
39	Диван	шт.	1	1000000	1000000
40	Диван	шт.	1	1000000	1000000
41	Диван	шт.	1	1000000	1000000
42	Диван	шт.	1	1000000	1000000
43	Диван	шт.	1	1000000	1000000
44	Диван	шт.	1	1000000	1000000
45	Диван	шт.	1	1000000	1000000
46	Диван	шт.	1	1000000	1000000
47	Диван	шт.	1	1000000	1000000
48	Диван	шт.	1	1000000	1000000
49	Диван	шт.	1	1000000	1000000
50	Диван	шт.	1	1000000	1000000
51	Диван	шт.	1	1000000	1000000
52	Диван	шт.	1	1000000	1000000
53	Диван	шт.	1	1000000	1000000
54	Диван	шт.	1	1000000	1000000
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59	Диван	шт.	1	1000000	1000000
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61	Диван	шт.	1	1000000	1000000
62	Диван	шт.	1	1000000	1000000
63	Диван	шт.	1	1000000	1000000

Key: (1). Catalyst. (2). Solvent. (3). Concentration. (4). monomer. (5). catalyst. (6). Temperature. (7). Time hours. (8). Conversion. (9).  $\eta_{inh}$ . (10). inherent viscosity (11). Benzoyl peroxide. (12). Benzene. (13). Di-*n*-butylmagnesium.

FOOTNOTE 1. Conditions of polymerization as for methyl methacrylate.



[5] ENDFOOTNOTE.

14. Toluene; 15. Dipyrnyl magnesium; 16. Butyllithium.

FOOTNOTE. Conditions of polymerization as in [2]. ENDFOOTNOTE.

have 19.

At  $-60^{\circ}$  catalyst 14 and with benzoyl peroxide at  $60^{\circ}$  we obtained virtually polymers identical with respect to micro-tactic - predominantly syndiotactic structure (table). In PFMA, obtained on catalyst 15 at  $-50^{\circ}$  the content of isotactic triads (from 4 to 48) due to a reduction in the content of syndio- and heterotriads sharply is raised. In butyllithium at  $-50^{\circ}$  highly-isotactic PFMA, which contains 90% isotactic triads, is obtained.

#### EXPERIMENTAL RESULTS

By method NMR is studied micro-tactic of samples of poly(pentafluoromethyl methacrylate) PFMA synthesized by different methods. It is established that in the catalyst of dipiperidy, magnesium and with the radical polymerization are formed the polymers of predominantly syndiotactic structure. In the catalyst of dipyrnyl, magnesium is obtained atactic polymer with somewhat increased content of isotriads (48) in butyllithium highly isotactic PFMA which contains 90% isotactic triads is obtained.

Institute of petrochemical synthesis im. A. V. Topchiyev of the AS  
USSR.

It was received by the editorial staff 11 SEPT. 1970.

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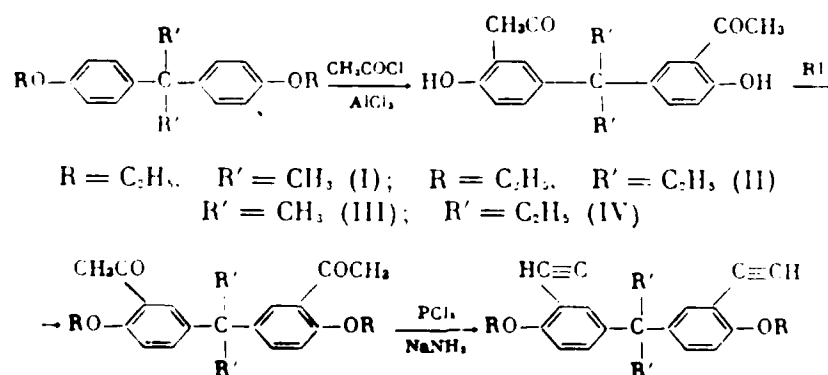
## SOLUBLE POLY-ACETYLENE OLIGOMERS WITH DIELECTRIC PROPERTIES.

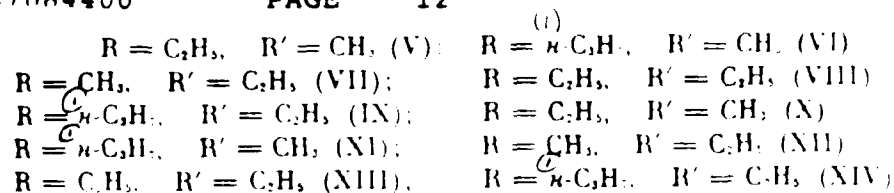
I. Ye. Sokolov, A. S. Zanina, I. L. Kotlyarevskiy.

Earlier [1-3] we showed that polyarylene-polyacetylene oligomers become soluble with the introduction into link of oligomer of branched alkane bridge between phenyl nuclei [1-3].

Purpose of this work - synthesis of diacetylene monomers, in which with preservation of alkane bridge between phenyl nuclei are introduced alkoxy groups into aromatic nucleus, obtaining of soluble oligomers on their basis and investigation of properties of these oligomers.

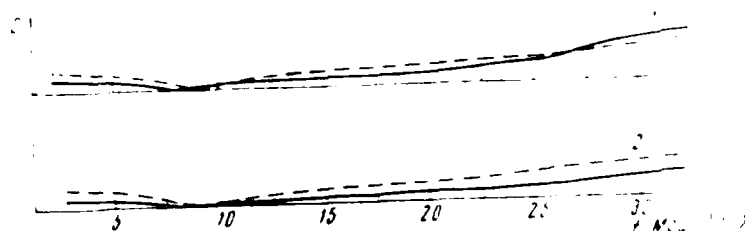
Synthesis of monomers was realized according to following diagram:





Key: (1). n.

Acetylation with I and II acetylchloride in presence of aluminum chloride in dichloroethane leads to obtaining of diacetyl derivatives of diphenylol propane and diphenylolpentane (III and IV) with output/yield 65.3 and 72.0%. Obtaining these products attests to the fact that in this reaction together with the acetylation the reaction of dealkylation [4] occurs.



Dependence of the capacities of samples XIII (1) and XV (2) on the frequency; broken line - capacity of instrument.

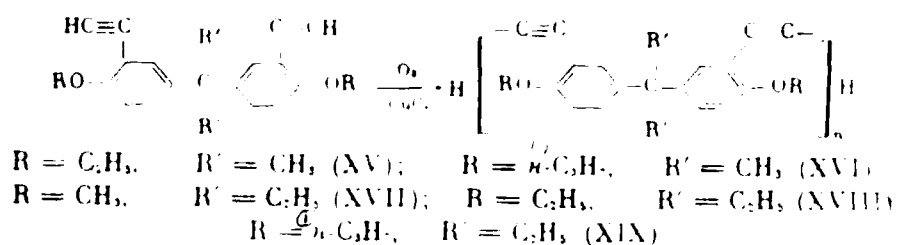
Key: (1) MHz.

Page 312.

Alkylation III and IV was conducted by alkyl iodides in medium of corresponding alcohol and in presence KOH. The outputs/yields of alkyl ethers/esters III and IV lie/rest within limits of 60-85%. Transition to the diethynyl derivatives of dialkyl ethers/esters of diphenylol propane and diphenylolpentane (V-IX) was realized with the aid of the reaction of chlorination and subsequent dehydrochlorination by sodium amide in liquid ammonia. The outputs/yields of diacetylenes (X-XIV) lie/rest within wider limits of -20-60%.

For X-XIV is characteristic presence in IR-spectrum of intensive absorption band in region  $3300\text{ cm}^{-1}$ , which testifies about presence of unsubstituted acetylene hydrogen.

Oligomers were obtained by reaction of oxidative polycondensation with quantitative output/yield during oxidation X-XIV in pyridine in presence CuCl in atmosphere of oxygen according to diagram



Key: n.

Oligomers XV-XIX are weakly-painted powders, soluble in series/number of organic solvents. The solubility of oligomers is increased with an increase in radicals R and R'. Thus, for example, if oligomer XV is soluble only in cyclohexanone and chloroform during the heating, then oligomer XIX is dissolved in the benzene, cyclohexanone, carbon tetrachloride, chloroform, dichloroethane at room temperature. At the same time in series/number XV-XIX the melting point of oligomers is lowered. If oligomer XV is softened at 250-260°, then oligomer XIX is melted in limits of 150-180°. The melting point of oligomers depends also on their molecular weight, which, in turn, can be varied, changing the conditions of reacting the oxidative polycondensation (Table 1).

Specially conducted investigation based on example of obtaining oligomer XV showed that while conducting of oxidative polycondensation in pyridine with catalytic quantities CuCl degree of polycondensation n XV was equal to 5, during application of threefold excess of pyridine  $n=2$ , addition of tetramethylenediamine leads to XV with  $n=10$ .

Table 1. Dependence of molecular weight of oligomer XV on quantity of pyridine <sup>1</sup>.

FOOTNOTE <sup>1</sup>. Quantity of diacetylene X - 500, CuCl - 50 mg.

ENDFOOTNOTE.

Количество пиридина (1)	Молекулярный вес (2)	Степень поликонденсации (3)	Т. пл., °C (4)
50	1630	5	170-180
150 (6)	700	2	70-80
50 + 0.3 г TMOCl	3317	10	190-205

Key: (1). Quantity of pyridine, ml. (2). Mol. weight. (3). Degree of polycondensation. (4). Melting point. (5). g.

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FOOTNOTE <sup>2</sup>. Melting point of monomer X 91-93°. ENDFOOTNOTE.

Table 2. Dielectric properties XV and XVIII.

Олигомеры (1)	$\epsilon$	$\operatorname{tg} \delta$	$U_{\text{пр.}}$ кВ (2)	$f$ кГц (3)
XV	3.7	0.0075	$2.0 \cdot 10^6$	25
XVIII	3.6	0.0065	$2.0 \cdot 10^6$	20

Note.  $\epsilon$  - dielectric constant,  $\operatorname{tg} \delta$  - the loss tangent,  $U_{\text{пр.}}$  - breakdown voltage, V/cm,  $f$  - current frequency, kHz. Numerical values  $\epsilon$ ,  $\operatorname{tg} \delta$ ,  $U_{\text{пр.}}$  are neutralized/averaged on fifty samples.

Key: (1). Oligomers. (2).  $\frac{U}{V}$ /cm. (3). kHz.

During application of copper acetate in pyridine in presence of small quantity of methanol molecular weight XV is equal to 1697, in this case  $n=5$  and melting point of 175-187°.

Solutions of oligomers XV and XVIII easily will be brought in on surface of glass and metals and after solvent elimination do not settle into precipitate, but are formed clear sheets. During heating of films up to 200° for 1 hour their thermal stereopolymerization due to the break of triple bonds occurs, and films become nonmelting and undissolved. Films from oligomers XV and XVIII maintain/withstand heating up to 250°.

Adhesion of film to aluminum for XV, thoroughly heated 1 hour at 200°, is 160-200 kg/cm<sup>2</sup>. The dielectric properties XV and XVIII are given in Table 2.

Retention/maintaining stability of capacity at high frequencies (figure) is very interesting property of these films. As can be seen from the figure, is not observed changes of the capacity from the frequency within the limits from 20 kHz to 30 MHz.

#### Experimental part.

Acetylation of 2,2-bis(p'-ethoxy phenyl)propane (I). To the solution 20 g of I in 85 ml dry dichloroethane and 35 g CH<sub>3</sub>COCl during 0-2° and mixing they added in 1.5 hours of 61 g AlCl<sub>3</sub>. Reaction



mixture mixed 3 hours at 50°, they cooled and decomposed/expanded, pouring out into mixture HCl with ice. They extracted by benzene, the organic layer was washed by water, dried above CaCl<sub>2</sub>, after solvent elimination obtained 15 g of diketone III, output/yield 63.5%, melting point of 141-142° (CH<sub>3</sub>OH: benzene =3:1).

It is found, %: C 72.87; H 6.45. C<sub>11</sub>H<sub>10</sub>O<sub>4</sub>. It is calculated, %: C 73.06; H 6.45. Analogously from 20 g II was obtained 15.2 g of diketone IV; output/yield 72.0%, melting point of 153-154° (CH<sub>3</sub>OH: benzene =3:1).

It is found, %: C 74.05; H 6.97. C<sub>12</sub>H<sub>10</sub>O<sub>4</sub>. It is calculated, %: C 74.09; H 7.11.

Alkylation of 2,2-bis-(3'-acetyl-4'-hydroxyphenyl)propane. To the mixture 12 g of diketone III and 4.3 g KOH in 200 ml C<sub>2</sub>H<sub>5</sub>OH they added in 15 min. 24 g C<sub>2</sub>H<sub>5</sub>I, mixed at 70° during 10 hours, they cooled, extracted by ether/ester, the ether extract they washed in water and dried CaCl<sub>2</sub>. After the removal of ether/ester obtained 7.0 g V, output/yield 63.5%, melting point of 78.5-7.95° (from alcohol).

It is found, %: C 74.88; H 7.55. C<sub>12</sub>H<sub>10</sub>O<sub>4</sub>. It is calculated, %: C 74.97; H 7.66. Under the analogous conditions dialkoxydiketones XI-IX (Table 3) were obtained.

Table 3. Output/yield and the constant of dialkoxydiketones and diacetylenes.

Монимер (1)	Выход, % (2)	Т. пл., °C (3)	(4) Найдепо %		Брутто-Формула (5)	Вычислено, % (6)	
			С	Н		С	Н
Диаалкоксидикетоны (7)							
IV <sup>1</sup>	74,2	41—42	75,11	8,21	C <sub>25</sub> H <sub>20</sub> O <sub>4</sub>	75,72	8,13
VII <sup>2</sup>	83,7	86—87	74,80	7,53	C <sub>25</sub> H <sub>20</sub> O <sub>4</sub>	74,97	7,66
VIII	85,6	114,5—116	75,41	8,21	C <sub>25</sub> H <sub>20</sub> O <sub>4</sub>	75,7	8,13
IX	60,5	75—76	76,23	8,69	C <sub>25</sub> H <sub>20</sub> O <sub>4</sub>	76,38	8,55
Диацетилены (8)							
XI <sup>3</sup>	60,0	—	83,03	7,91	C <sub>25</sub> H <sub>20</sub> O <sub>4</sub>	83,29	7,85
XII	31,4	142	82,98	7,30	C <sub>25</sub> H <sub>20</sub> O <sub>4</sub>	83,10	7,28
XIII	19,25	122,5—123	83,49	7,99	C <sub>25</sub> H <sub>20</sub> O <sub>4</sub>	83,29	7,83
XIV	27,6	85—86	83,54	8,56	C <sub>25</sub> H <sub>20</sub> O <sub>4</sub>	83,46	8,30

Key: (1). Monomer. (2). Output/yield. (3). Melting point. (4). It is found. (5). Sum formula. (6). It is calculated. (7). Dialkoxydiketones. (8). Diacetylenes.

FOOTNOTE <sup>1</sup>. Boiling point at 275-277/2 mm.

<sup>2</sup>. VII was obtained upon alkylation by IV dimethylsulfate in water.

<sup>3</sup>. XI - liquid is decomposed/expanded with distillation, it is purified chromatographically. ENDFOOTNOTE.

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Obtaining 2,2-bis-(3'-ethynyl-4'-ethoxyphenyl)propane.

Chlorination of 2,2-bis-(3'-acetyl-4'-ethoxyphenyl)propane. 12.4 g of diketone of the III in 100 g dry benzene heated 1 hour with 17 g PCl<sub>5</sub>, at 70°. They decomposed/expanded reaction mixture, pouring out to ice, extracted by ether/ester. They washed organic layer in water,

dried above  $\text{CaCl}_2$ , and introduced into the reaction of dehydrochlorination, without separating/liberating obtained chlorides.

Dehydrochlorination. To amide of sodium (of 20 g Na in 500 ml  $\text{NH}_3$ ) was added the ether/ester-benzene solution of the mixture of chlorides and were mixed 4 hours. They decomposed/expanded, adding 40 g  $\text{NH}_4\text{Cl}$ , 200 ethers/esters even 200 ml of water. They washed organic layer in water, dried above  $\text{CaCl}_2$ . Obtained 4.9 g of diacetylene X, output/yield 45.3% (to diketone V); melting point of  $91-93^\circ$  (from alcohol).

It is found, %: C 93.35; H 6.68.  $\text{C}_{12}\text{H}_{10}\text{O}_2$ . It is calculated, %: C 93.40; H 6.60. Diacetylenes XI-XIV were obtained in a similar manner (Table 3).

Oxidative polycondensation of 2,2-bis-(3'-ethynyl-4'-ethoxyphenyl)propane. They shook the solution 0.5 g of diacetylene X in 50 mm dry pyridine in the weft to the stop of the absorption of oxygen in the presence 0.05 g  $\text{CuCl}$ , then they poured out reaction mixture into the water, the fallen precipitate filtered out, washed by water and  $\text{HCl}$  (1:9), by alcohol and by ether/ester. Was obtained oligomer XV; output/yield quantitative, melting point of  $170-180^\circ$ , molecular weight 1630.

It is found, %: C 83.74; H 6.96.  $\text{C}_{12}\text{H}_{10}\text{O}_2$ . It is calculated, %: C 83.60; H 6.71. Oligomers XVI-XIX are obtained employing the

same procedure, their characteristic is given in Table 4, outputs/yields are quantitative.

#### Conclusions.

Method of synthesis of soluble poly-acetylene oligomers, which possess film-forming and dielectric properties, is developed.

Table 4. Characteristic of oligomers XVI-XIX.

Олиго- меры (1)	Т. пл., °C (2)	Мол. вес (3)	(4) Найдено, %		Брутто-фор- мула (5)	(6) Вычислено, %	
			C	H		C	H
XIV	115-130	1450	83.34	7.96	$C_{15}H_{16}O_2$	83.76	7.31
XVII	250-260	2000	83.42	6.78	$C_{15}H_{22}O_2$	83.60	6.71
XVIII	168-175	1800	83.29	7.76	$C_{25}H_{26}O_2$	83.76	7.31
XIX	150-180	1950	83.57	8.10	$C_{27}H_{30}O_2$	83.90	7.82

Key: (1). Oligomers. (2). Melting point. (3). Mol. weight. (4). It is found. (5). Sum formula. (6). It is calculated.

Institute of chemical kinetics and SO AN SSSR [Siberian Department of the Academy of Sciences of the USSR] burning.

It was received by the editorial staff 21 SEPT. 1970.

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